

# UK Patent Application (12) GB (19) (11) 2 231 572 A (13)

(43) Date of A publication 21.11.1990

(21) Application No 9007466.7	(51) INT CL <sup>a</sup> C09D 11/02, B42D 15/00, C08K 3/08 9/04 // B41M 3/14
(22) Date of filing 03.04.1990	
(30) Priority data (31) 8908049 (32) 11.04.1989 (33) GB	(52) UK CL (Edition K) C3K KDA K101 B6A AC21 AC31 ATC C3L LDP C3W W217 W222 W225 W228 W304 W315 U1S S1390 S2271 S2272 S3071
(71) Applicant The De La Rue Company p.l.c. (Incorporated in the United Kingdom)  De La Rue House, 3/5 Burlington Gardens, London, W1A 1DL, United Kingdom	(56) Documents cited GB 1452000 A US 3692731 A
(72) Inventors Julian Holloway Malcolm Swales Knight	(58) Field of search UK CL (Edition K) C3K KDA KJA KXX, C3L LDM LDP, C3V VAD VAE Online databases: WPI
(74) Agent and/or Address for Service Gill Jennings & Every 53-64 Chancery Lane, London, WC2A 1HN, United Kingdom	

## (54) Ink composition and printed security documents

(57) An ink composition comprises (a) colouring matter, (b) discrete coated particles of a material having a reflective metallic appearance, the coating comprising a translucent protective material such that, on immersion of the coated particles in 10% aqueous NaOH at 25°C, the coated material is protected for at least 30 min, together with (c) an ink vehicle.

The ink can be used to print a security document.

Further, a security document having a coloured reflective metallic appearance, comprises discrete coated particles as defined above and a colouring agent.

Two inks may be printed, of which one comprises the discrete coated particles and the other is coloured, in which the second ink is translucent and/or does not fully overlie the first ink.

GB 2 231 572 A

INK COMPOSITION AND PRINTED SECURITY DOCUMENTS

This invention relates to metallic inks and to their use in security documents.

Printing inks which display a metallic appearance 5 are well known; commonly these comprise finely particulate metals or metallic compounds.

The stability requirements of inks used in currency printing are stringent, because any significant variation of appearance during the life of the currency item is 10 unacceptable and would lead to a central bank refusing to accept it as legal tender. Confusion with counterfeits is also possible.

The use of metallic inks provides a useful security feature, as their reproduction is more difficult than 15 conventional colours. Metallic print is especially resistant to colour photocopying.

Inks having, say, a golden appearance would add both attractiveness and security to a banknote. Despite various attempts in the past, no banknote has yet been 20 viably printed with a golden ink. It is critical that all parts of a banknote last for its life which, desirably, is tens of years. They must therefore be atmosphere, solvent, acid and alkali-resistant.

Gold inks are well known for offset lithographic and 25 letterpress printing of non-security matter such as greeting cards. Such gold inks comprise bronze flake or powder. For security and currency printing, however, bronze-containing gold-like inks are unsatisfactory because the gold-like appearance changes in circulation 30 and on handling, due to tarnishing effects which progressively and irreversibly result in a black appearance. This deterioration is commonly ascribed to reaction of the bronze with atmospheric sulphur-containing gases. Cost prohibits the use of gold flake 35 instead of bronze.

According to a first aspect of the present invention, an ink formulation contains:

- (a) colouring matter;
- 5 (b) discrete coated particles of a material having a reflective metallic appearance, the coating comprising a substantially continuous translucent film-forming protective material such that, on immersion of the coated particles in 10% aqueous NaOH at 25°C, the coated material is protected for at least 30 min, when formulated into an ink formulation as herein described, together with
- 10 (c) an ink vehicle, usually including a drier compound.

15 According to a second aspect of this invention, a security document having a coloured reflective metallic appearance comprises discrete coated particles as defined above and a colouring agent.

20 Component (a) of the novel ink, the colouring matter, has or may produce, as by ultraviolet or near infrared irradiation, a colour in the visible region of the spectrum; for a gold effect, the chosen colour will be yellow or orange. Other colorants may be added, leading to a wide variety of attractive colours including 25 blues, greens, reds, magentas and cyans. For ease of formulation, an offset lithographic ink which has the correct hue is preferably chosen as the means of introducing compound (a), e.g. in an amount of 10 to 40% w/w.

30 Examples of suitable colouring matter are Colour Index Pigments (Red, Yellow, Green or Blue). The preferred colouring materials are dyes or, preferably, pigments of a range of transparencies, exhibiting good fastness to light and chemicals consistent with inks used 35 in security printing. The colouring matter or pigment is

in particulate form, the particles being, for example, from 0.05  $\mu\text{m}$  up to 1  $\mu\text{m}$ , e.g. about 0.1  $\mu\text{m}$ , in size.

Component (b) is a reflective metallic component, i.e. any metal, metal alloy or metallic compound that 5 exhibits or is capable of exhibiting the sheen of a metal in common usage; such metals include aluminium, nickel, copper, chromium, silver, zinc, tin, steels, bronzes and brasses. Aluminium is preferred. Nickel-chrome is an alternative. Silver is generally unnecessarily 10 expensive. The metallic component may be inherently uncoloured or coloured to the eye. Preferably the metal possesses a bright metallic lustre.

The particles of the finely-divided metallic compound may range in size from 0.1  $\mu\text{m}$  to, preferably, a 15 maximum size of 20  $\mu\text{m}$ . The particulate metallic compounds may be in the form of powder or flakes and may be incorporated in the composition in the form of pre-prepared metallic inks. Some metallic inks may include a resin or other component which can act as an 20 inert component of the novel composition. The use of an offset printing ink having a silver appearance, e.g. in an amount of 30 to 60% w/w, facilitates the formulation of an ink of the invention.

Preferably, for use as a metallic ink having a 25 silver-like appearance, component (b) comprises aluminium flakes. Such flakes may have a width about ten times their thickness, and are generally a factor of 10-100 larger than the particles of colouring matter.

A typical formulation for an offset lithographic 30 metallic printing ink having the desired metallic/silver appearance is (% by weight):

	Coated Metallic Flake	40-45, e.g. 45%
	Petroleum Distillate	2-8, e.g. 3%
	(Solventless) Long Oil Alkyd varnish of medium viscosity	15-35, e.g. 24%
5	Medium-to-Short Oil Alkyd of high viscosity	10-20, e.g. 14%
	Tack Modifying additive	0-20, e.g. 9%
	Fluon Powder 170	0-20, e.g. 3%
	Mixed Drier Compound	0-20, e.g. 2%

10        The function of the coating on the metallic  
particles is to impart protection. The coating must  
therefore be durable and not dissolve when the ink is  
formulated. The protective coating should not be tacky  
under normal conditions, otherwise the protected  
15      particles will be liable to agglomeration; the coated  
particles are discrete. The coating should form a  
continuous film around the particles. The coating must  
be translucent, allowing reflected light to emerge from  
the metal. It may be completely transparent, which is  
20      preferred.

20        In order to test for satisfactory coating, the  
particles are blended into a lithographic ink and printed  
on an alkali-resistant paper. The ink is then subjected  
to a severe test by immersion in 10% aqueous sodium  
25      hydroxide solution for a period of 30 minutes at 25°C.  
The protected particles exhibit either their original  
metallic appearance or a grey appearance.

30        Unprotected aluminium particles exhibit no metallic  
or grey appearance. This is normally because the  
aluminium pigment has dissolved in the alkali. It is as  
desirable to prevent this as it is to ensure that other  
metals, e.g. tin, silver, stainless steel, zinc or  
chromium-steel, are protected from reagents which will  
cause deterioration of the particles, including common  
35      acids, alkalis or oxidising agents.

The metallic particles therefore bear a polymeric protective coating which is applied prior to their incorporation into the ink formulation. This coating remains around the particles when they are incorporated 5 into an ink vehicle. The coating will normally be less than 10 nm thick. The coated particles preferably have a size of the order of 3  $\mu\text{m}$  x 6  $\mu\text{m}$  by 0.02  $\mu\text{m}$ .

The protective coating will normally be transparent or translucent, and colourless. It may comprise a 10 thermosetting polymer such as an epoxy resin, a tough thermoplastic polymer such as high molecular weight polyvinyl chloride, a polyacrylate or polystyrene, or another suitable resin composition. Preferably, aluminium flake particles are coated within a protective 15 binder of polyethylene or polyester. Resin-protected aluminium-based pigments are available commercially from Silberline Ltd.

Component (c), the vehicle, may be conventional for a lithographic or other ink for printing on to a 20 substrate to be used in a security document. The vehicle may constitute 50 to 95% w/w of the composition, and may include diluents, extenders, alkyds, driers and any other components which are known to have properties suitable to impart the desired rheological and/or other 25 characteristics; examples are bentones and polyethylene waxes.

An optional but preferred component of the permanently coloured novel composition is a luminescent agent. A suitable such material normally comprises 30 daylight-coloured or colourless fluorescing or phosphorescing, as by ultraviolet or infrared irradiation, additives. Examples of luminescent materials are given in EP-A-0253543. Phosphorescent materials may be mixed therewith, provided they are of 35 suitable particle size. The particle size is preferably

0.01 to 1  $\mu\text{m}$ . The amount of the luminescent agent used in an ink of the invention is, for example, 1 to 10% w/w.

The emission of the luminescent material may, but need not, match the daylight colour of the pigment toner.

5. Its presence facilitates authentication, when excited by a suitable source of ultraviolet or near infrared light.

A description of coloured and metallic offset lithographic inks will be found in "The Printing Ink Manual" (1979, Northwood Publications Ltd), "Inks for the 10 Minor Printing Processes and Specialised Applications" (E.A.Apps, 1966, Leonard Hill (Books) Ltd), and in the Pantone range available from Pantone Inc., 55 Knickerbocker Road, Moonachie, New Jersey 07074, U.S.A.

Fluorescent agents suitable for the invention are 15 reviewed in "Colour Index" (Third Edition, 1971, Volumes 2,6,7, The Society of Dyers and Colourists), "Luminsecence of Liquids and Solids" (P. Pringsheim and M. Vogel, 1943, Interscience Publishers Inc., New York), and in Kirk-Othmer's "Encyclopaedia of Chemical 20 Technology" (Volumes 9,12, Second Edition, 1966, Interscience Publishers Inc. New York).

A preferred composition of the invention may be prepared by mixing the luminescent agent with a coloured ink and a metallic ink, in which case it is not always 25 necessary to add further components. However, up to 60% w/w may be added, including up to 5 to 10% w/w of a solvent and/or other additives which may facilitate mixing of the respective inks.

Alternatively, an ink of the invention may be 30 prepared by a process comprising the following steps:

- (1) Pre-dispersion and triple-roll milling of the coloured toning pigment in grinding medium;
- (2) mixing/blending of other powder components with the pre-ground pigment and additives; followed by

(3) mixing and homogenising with the pre-wetted and pre-coated metallic flake.

The finished (final) ink should not be subjected to milling on a triple-roll mill, as this would result in 5 degradation of the metallic appearance of the dry print. The ingredients are intimately mixed by gently stirring and mixing.

Inks of the invention are primarily intended to be printed on to security documents. In this context, the 10 substrates used for printing are generally paper, including rag paper, preferably currency grade paper, plastic-coated or laminated paper, and plastics such as, for example, bank cardgrade PVC, or plastic paper, e.g. non-woven plastic paper. Articles bearing security 15 printing include banknotes, currency, travellers' cheques, cheques, bonds, certificates, ownership documents, passports, identity cards, credit cards, charge cards, access cards and smart cards, and also tickets, licences and stamps.

20 Security documents normally have different types of printing present selected from intaglio, offset lithographic and letterpress printing. A coloured metallic ink of the invention will normally be used in addition to/beside security printed areas in a variety of 25 colours. Rainbow-printing techniques are often used in security documents. After lithographic printing, the gloss of the coloured metallic ink may be improved by subjecting the printed area to the calendaring conditions of intaglio printing.

30 Security documents of the invention, especially currency, exhibit improved ageing-stability and laundering-stability, while providing, say, a golden hue or lustre without undue cost.

One embodiment of a security document of the 35 invention comprises a substrate and, printed thereon, in

order, first and second inks of which one comprises discrete coated particles as defined above for component (b), and the other is coloured, in which the second ink is translucent and/or does not fully overlie the first 5 ink, whereby the appearance of the document, at a normal viewing distance of about 300 mm (unmagnified), is of a coloured, reflective metal. Thus, for example, if the first and second inks were printed as multiple parallel bars of equal width, the width of a bar should be less 10 than 0.2 mm, preferably less than 0.15 mm, and most preferably less than 0.1, mm. Designs other than parallel lines include equivalent visual constructions, including half-tone screen effects and random mottle effects. Such half-tone screens may typically have a 15 resolution of about 150 lines per inch (6 lines per mm) and have a range of 20 to 80 . dot coverage of ink.

The coloured lithographic ink may be any lithographic printing ink. However, the second ink must have adequate translucency or be printed with sufficient 20 voids so as to allow the first ink's colour to be seen. The thickness of ink may also be controlled within the usual operating printing parameters to increase or decrease the translucency. Typical lithographic printing thicknesses are in the range of 0.5 to 2.0  $\mu$ m.

25 The metallic ink is preferably applied as the second ink, especially if the security document is subjected to intaglio conditions. While the first printing will usually be lithographic, the second may not have to be if the second ink is metallic. As appropriate, standard 30 offset lithographic printing methods, such as are used in the security printing industry, are employed. After lithographic printing, which normally occurs during one

printing run of the offset press, the inks are allowed to dry, resulting in printing of coloured metallic appearance.

Rainbow printing is widely used in the security industry. The method involves supplying two differently-coloured inks in adjacent sections of a printing press ink duct. Owing to the oscillation of the rollers in the inking train, the two inks mix on the rollers so that the printed document bears a band of mixed ink. The colour of the mixed ink at any point in the band varies depending on the ratio of pure inks and continuously varies across the band.

Examples of combinations of coloured inks of the invention which would allow rainbow printing effects are (in adjacent ink reservoirs):

- (1) invention ink: conventional metallic ink (preferably of comparable durability);
- (2) invention ink of first colour; invention ink of second colour;
- (3) invention ink: conventional coloured ink;
- (4) invention ink: luminescent ink;
- (5) invention ink: metallic fluorescent ink;
- (6) luminescent invention ink; metallic fluorescent ink; and
- (7) luminescent invention ink; invisible fluorescent ink.

The inks of the invention may be used, for example, in the printing of intersecting colour patterns, e.g. duplex and triplex patterns, and in see-through features and print-through features.

It is common for many types of security documents to receive printing by intaglio. Such intaglio printing of one or more colours is applied after lithographic printing.

When the coloured metallic printing of this invention (whether formed by a single lithographic print impression of a coloured metallic ink or by two lithographic printings, respectively of metallic ink and 5 coloured ink) is placed on a security document it has been found that the specular reflectance (i.e. gloss) can be further enhanced considerably. This is achieved by subjecting the coloured protected metallic printed area to calendaring conditions. Preferably such conditions 10 are created when the document is subject to security printing by intaglio. An area of the intaglio plate corresponding to the printed area is arranged to be smooth, so that a polishing action occurs.

For the combination of lithographic inks it has been 15 found that better gloss after intaglio calendaring is achieved when the metallic ink is deposited as the second, uppermost ink.

Using such intaglio calendaring methods, the specular reflectance as measured by a gloss meter has 20 doubled, thus greatly enhancing the metallic visual appeal and making counterfeiting more difficult.

A further security enhancement may be made by including engraved matter in the areas of the intaglio press corresponding to the coloured metallic printing. 25 With inking, a coloured intaglio image may be applied on top of the coloured metallic area. In the absence of inking, transitory images such as latent or transient embossed image patterns may be applied.

The second ink is preferably opaque, in which case 30 it must be provided in a discontinuous pattern with respect to the first ink (which may itself cover all or only part, e.g. in a suitable pattern, of the substrate). Thus, while the overlap of the inks may be complete, the second ink, i.e. the topmost layer, is preferably printed 35 in a partially overlapping pattern.

The pattern may be a screen pattern, e.g. a fine line or grid pattern, e.g. a 50% half-tone dot pattern. Fine-line patterning adds further security against photographic or laser scanning reproduction. This effect 5 may be enhanced by making either or both of the coloured ink and the metallic ink fluorescent.

Alternatively, anti-photoreproduction measures may be taken by causing the upper metallic ink to be printed in stripes over the coloured ink. As another alternative 10 to a screen pattern, other patterns may be employed such as parallel or regularly-curved fine lines.

The percentage of the area of the first ink or of the total area of the substrate covered by the second ink may vary from 10 to 95%, or greater, and is preferably 30 15 to 70%. A further feature may be added by making the percentage area vary such as in a half-tone reproduction of a line drawing. This gives the ability to make a metallic image on security base paper.

The effect of the combination of metallic and 20 coloured inks is to provide a cost-effective means of providing coloured metallic printing of improved attractiveness, while also making counterfeiting more difficult than hitherto.

The appearance of the printed area is such that the 25 inherent hue of the reflective metal is modified by the colouring agent whether pigment or dye. Generally this will mean imparting a distinctly different colour to the metal but, alternatively, the colouring agent may be used to enhance the inherent colour of the metal.

30 The visual appearance of a security document of the invention, from a normal viewing distance of approx. 0.4 m, is of a coloured metallic finish. Under magnification, when a non-overlapping pattern of the second ink is used, the colour is seen to comprise 35 discrete abutting portions of the first and second inks.

For example, when a silver metallic aluminium-based ink is printed in a dot pattern corresponding to a 50% fine-line half-tone screen, on a yellow ink, and then is viewed from 0.1 m or more, the differently-printed areas 5 apparently merge. Not only does the metallic finish provide counterfeiting difficulties, but the screening effect makes detection readily detectable under slight magnification.

A particular security document of this invention may 10 comprise, for example, a yellow or silver ink overprinted by a translucent or patterned ink of the invention which is metallic and coloured, e.g. having a gold effect (without using bronze or gold itself), on a banknote substrate.

15 The following Examples illustrate the invention.

Example 1 Gold Lithographic Ink Formulation

Yellow Pigment	10.0 g
Luminescer	4.5 g
Epoxy resin-coated metallic (Al) flake	5.0 g
20 Ink vehicle, driers etc.	80.5 g

Example 2 Green Lithographic Ink Formulation

Green Pigment	6.0 g
Luminescer	6.0 g
Polyethylene-coated metallic (Al) flake	5.0 g
25 Ink vehicle	83.0 g

Example 3 Blue Lithographic Ink Formulation

Blue Pigment	4.0 g
Luminescer	14.0 g
Polyester-coated metallic (Al) flake	4.0 g
30 Ink vehicle	78.0 g

Example 4 Violet Lithographic Ink Formulation

Violet Pigment	4.0 g
Luminescer	14.0 g
Polyacrylate-coated metallic (Al) flake	4.0 g
35 Ink vehicle	78.0 g

Example 5

A banknote base paper including a metallic security thread was printed, by offset lithography, with a fluorescent, yellow lithographic ink and, over the yellow ink, 5 a translucent polymer-coated aluminium flake-containing ink, silvery-metallic in appearance. The metallic ink was printed in a series of lines of equal width, and spacing of the order of 100  $\mu\text{m}$ , in grids of varying orientations.

10 The two inks were applied during a single pass through a multicolour offset press. At the same time, other lithographic security printing was applied to other areas of the substrate. After allowing the offset inks to dry, the printed substrate was subjected to intaglio 15 printing in a multicolour intaglio press.

Some of the areas on the intaglio plates had no engraving, but were smooth and ink-free. The resulting attractive golden metallic area had enhanced specular reflectance. The area is very difficult to counterfeit 20 by photographic means because of the combination of specular reflectance from the metal; the fine-line pattern potentially creates Moiré effects an half-tone screening production.

Example 6

25 A banknote rag base paper was printed by the procedure of Example 5, except that the first ink was a fluorescent, green lithographic ink, the metallic ink was printed, in an area having a diameter of approximately 20 mm, and one intaglio plate had an engraved image designed 30 to fit within the metallic area.

On intaglio printing the metallic area with the uninked engraving, a latent image was formed within the metallic area. The areas of the metallic area not corresponding to the engraving were polished by the 35 intaglio printing conditions.

The resulting attractive green metallic area had enhanced specular reflectance, and contained a latent image. The area was very difficult to counterfeit by photographic means because of the combination of specular reflectance from the metal and the variable viewing angle of the embossment.

Example 7

A cheque base paper was printed, by the procedure of Example 5, except that the first ink was a violet 10 lithographic ink and the translucent metallic ink was printed in the form of a double border line, 500  $\mu\text{m}$  wide. On intaglio printing, the areas of the metallic ink were polished. The resulting attractive violet metallic lines had enhanced specular reflectance.

Example 8

A share certificate base paper was printed by the procedure of Example 5, except that the first ink was a blue lithographic ink in the form of a medallion, the metallic ink overlapped the medallion evenly, so as to 20 give an even border, and an engraved facial profile was located on the intaglio printing plates, causing an intaglio-inked impression to be formed at the centre of the medallion, well within the borders. On intaglio printing, the areas of the metallic ink were polished. 25 The resulting attractive blue metallic medallion was surrounded by a silver border and contained the facial profile.

Example 9

A banknote base paper was printed with a solid patch 30 of blue lithographic ink. On top of this was then printed, during the same printing run, a silver-appearance ink comprising coated particles, in the form of a half-tone pattern corresponding to a graphical number pattern. Because of the varying deposition of the 35 silver ink, the printed patch, after blind intaglio

calendaring, gave the number pattern in shades of blue. From a normal viewing distance, the halftone deposition pattern was not seen; the image appeared substantially continuous in shades of metallic blue.

5

10

15

20

25

30

35

CLAIMS

1. An ink composition comprising (a) colouring matter, (b) discrete coated particles of a material having a reflective metallic appearance, the coating comprising a 5 translucent protective material such that, on immersion of the coated particles in 10% aqueous NaOH at 25°C, the coated material is protected for at least 30 min, together with (c) an ink vehicle.
2. An ink according to claim 1, in which the metallic 10 material is aluminium.
3. An ink according to claim 1 or claim 2, in which the metallic material is in the form of flakes.
4. An ink according to any preceding claim, in which the particles are no more than 20 µm in size.
5. An ink according to any preceding claim, which 15 comprises 1 to 10% w/w of the particles.
6. An ink according to any preceding claim, which comprises 1 to 20% w/w of the colouring matter.
7. An ink according to any preceding claim, in which 20 the vehicle includes an ink drier.
8. An ink according to any preceding claim, in which the colouring matter is yellow or orange.
9. An ink according to any preceding claim, which additionally comprises a luminescent agent.
10. An ink according to claim 9, which comprises 1 to 25 20% w/w of the luminescent agent.
11. A security document printed with an ink according to any preceding claim.
12. A security document having a coloured reflective 30 metallic appearance, comprising discrete coated particles as defined in any of claims 1 to 4 and a colouring agent.
13. A security document according to claim 12, comprising a substrate and, printed thereon, in order, first and second inks of which one comprises the discrete 35 coated particles and the other is coloured, in which the

second ink is translucent and/or does not fully overlie the first ink.

14. A security document according to claim 13, in which the first ink is coloured and the second ink comprises  
5 the discrete coated particles.

15. A security document according to claim 13 or claim 14, in which the second ink is provided in a fine-line or grid pattern.

16. A security document according to claim 15, in which  
10 the pattern is a half-tone dot pattern.

17. A security document according to any of claims 13 to 16, in which the second ink is opaque.

18. A security document according to any of claims 13 to 17, in which the second ink overlies 30 to 70% of the  
15 first ink.

19. A security document according to any of claims 13 to 18, in which either or each ink has one or more of the characteristics defined in any of claims 6 to 10.

20. A security document according to claim 12, which  
20 has one or more of the characteristics defined in any of claims 7 to 10.

21. A security document according to any of claims 12 to 20, which has been subjected to intaglio printing.

22. A security document according to any of claims 11  
25 to 21, in which the printed area has been calendared, to enhance the specular reflectance.